[1] Measurement of Radionuclides Using Ion Chromatography and Flow-Cell Scintillation Counting With Pulse Shape Discrimination For ER/WM Applications

R. A. Fjeld (fjeld@clemson.edu; 864-656-5569)
T. A. DeVol (tim.devol@ces.clemson.edu; 864-656-1014)
J. E. Roane (jroane@clemson.edu; 864-656-1530)
K. H. Hastie (khawtho@clemson.edu; 864-656-7239)
Clemson University
Clemson, SC 29634-0919

J. D. Leyba (john.leyba@srs.gov; 803-725-4180)
Westinghouse Savannah River Co.
Aiken, SC 29803

Introduction

Radiological characterization and monitoring is an important component of environmental management activities throughout the Department of Energy complex. Radionuclides which cannot easily be detected by gamma-ray spectroscopy such as pure beta emitters and transuranics pose special problems because their quantification generally requires labor intensive radiochemical separations procedures that are time consuming and not practical for field applications.

Approach

This project is focused on a technology that can measure transuranics and pure beta emitters relatively quickly and has the potential of being field deployable. The technology combines ion exchange liquid chromatography and on-line alpha/beta pulse shape discriminating scintillation counting resulting in simultaneous alpha and beta chromatograms. A schematic block diagram of the technology can be seen in Figure 1. It is capable of measuring pure beta emitters such as ^{90}Sr, ^{99}Tc and ^{63}Ni and actinides/transuranics such as ^{232}Th, ^{233}U, ^{237}Np, ^{239}Pu, ^{241}Am and ^{244}Cm in aqueous samples. Sample processing protocols are being developed for processing soil, groundwater, and waste tank supernatant.

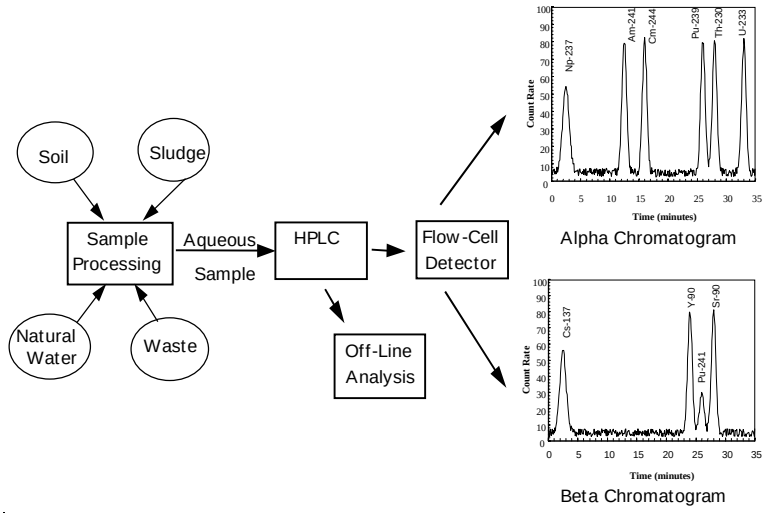

Figure 1. A schematic block diagram of the separation and detection technology

Project Objectives and Description

The project has three main objectives: (1) to develop a low background, pulse shape discriminating, flow-cell detector, (2) to identify chemical and radiological interferences, and (3) to develop protocols for processing waste and/or environmental samples. The project is focused on sample types and radionuclides that are relevant in environmental restoration and waste management applications.

The analysis technique combines ion exchange liquid chromatography and on-line scintillation counting. Radionuclides in ionic form in an aqueous solution are concentrated on an ion exchange column and subsequently removed to a separation column with chemical eluents. Through the selection and sequencing of the eluents, chromatographic separation of the constituents is achieved. A chromatogram of radioactive constituents is then produced by an on-line, flow through scintillation detector. The flow-cell detector employs pulse shape discrimination to distinguish between alpha and beta particles and to enable the display of separate chromatograms for alpha and beta emitting radionuclides. For very low-level applications, fractions containing selected radioelements can be collected and counted off-line.

Results and Accomplishments

Task 1. Detector Development. A suite of potential scintillation materials were tested and evaluated for their pulse shape discriminating ability with both a heterogeneous and a homogeneous flow-cell detection system. For the heterogeneous system, polymer-coated CsI:Tl was selected as the best scintillating material and incorporated into a prototype detector system. The prototype exceeded the project goals for minimum detectable activities for both alpha emitters (0.2 Bq vs the goal of 0.5 Bq) and beta emitters (0.9 Bq vs the goal of 5 Bq). A significant accomplishment is the successful collection and display of dual parameter (pulse height and pulse shape) data, which offers the promise of enhanced alpha/beta separation and a further lowering of detection limits, see Figure 2. The homogeneous flow-cell evaluations are still in progress. Figure 3 is an example of a pulse shape spectrum for the homogeneous flow-cell detector using Packard Ultima Gold AB scintillation cocktail. A summary of the heterogeneous results and the homogeneous results to date are listed in Table 1.

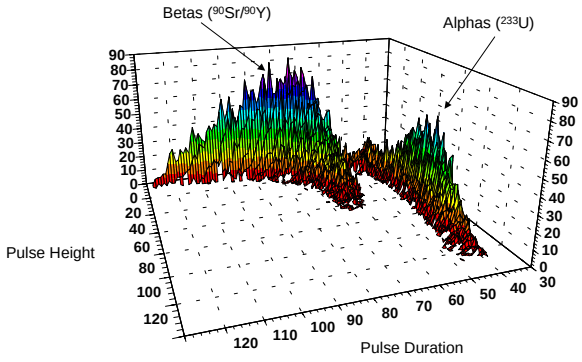

Figure 2. Heterogeous CsI:TI Dual Parameter Spectrum

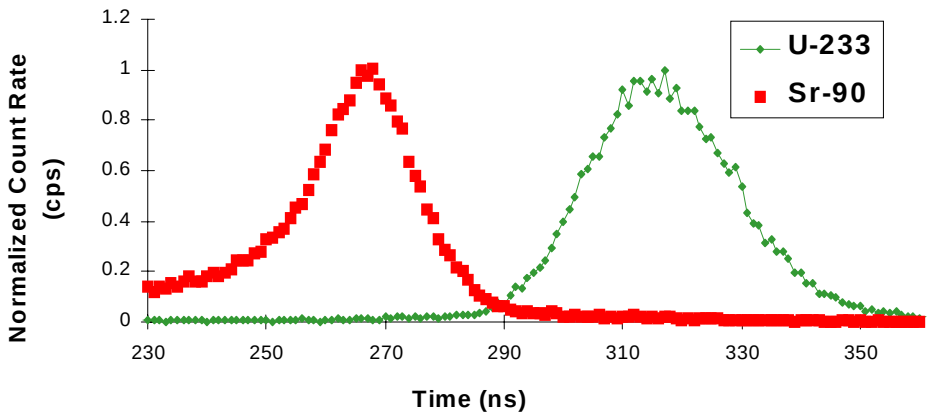

Figure 3. Pulse Shape Spectrum: Homogeneous Detector System.

Table 1. Results summary for Task 1 to date.

	Heterogeneous		Homogeneous		Goals	
	α	β	α	β	α	β
Detection efficiency (%)	65	53	99	64	70	50
Background (cpm)	0.25	12	2.4	27.6	0.5	10
Spillover	4.4	0.2	3.5	3.5	<5	<5
MDA (Bq)	0.2	0.9	0.26	1.04	0.5	5

Task 2. Identification of Interferences. Chemical and radiological constituents likely to be found in environmental and waste samples were tested to determine their potential for interfering with analyses. An example of this is summarized in Table 3. Baseline chemical concentrations were formulated for nine compounds containing various anions and cations found in environmental and waste samples. Chemical interferences were quantified through an operational parameter called the non-observable effects loading (NEL), which is the level below which an interference was not observed. NELs for detection efficiency and peak elution time were determined for the baseline compounds. The most problematic radiological interference was due to natural uranium and/or its decay products. Changing the ion chromatography elution scheme has mitigated these problems. Results are summarized in Table 4.

Table 2. Values of Non-observable Effects Loading (NEL) for the chemicals used in this study.

Chemical	Detector Efficiency Criterion µmoles	Peak Elution Criterion µmoles
$Al(NO_3)_3$	4	1
$Ca(NO_3)_2$	4	1
NaOH	140	140
$NaNO_3$	350	280
$NaHCO_3$	34	34
$NaNO_2$	430	700
Na_2SO_4	60*	60*
KCL	12*	12*
NaCl	160*	160*

Chemical	Detector Efficiency Criterion Activity, Bq	Peak Elution Criterion Activity, Bq
Uranium	5	1

Note: * denotes that the baseline mass loading for these chemicals did not affect detection efficiency or peak elution times.

Task 3. Development of Sample Processing Protocols. Protocols have been developed for analysis of environmental and waste samples such as groundwater, soil, and waste tank supernatant. Samples are typically completely digested using microwave-aided digestion. Presented in Figure 4 is the sample processing protocol developed for use with samples in complex sample matrices. An example of the results of the sample processing protocol is shown in Figure 5. Work is currently underway on the application of the protocols to soils spiked with ^{90}Sr, ^{233}U, ^{241}Am, and ^{244}Cm.

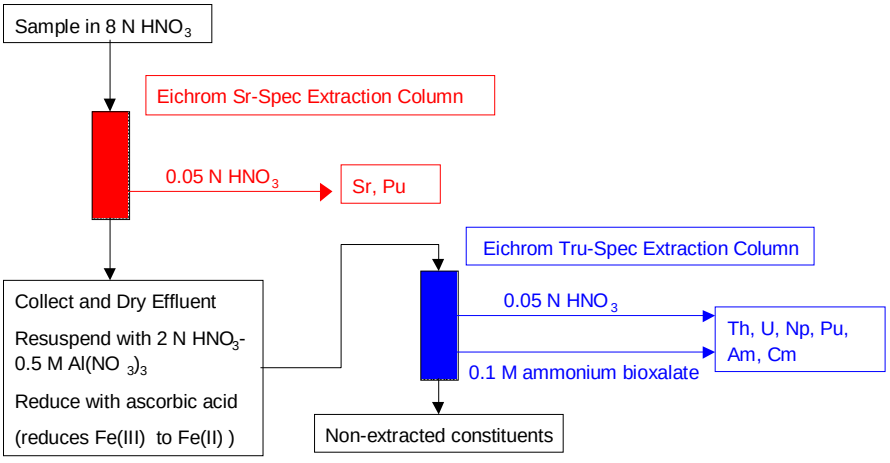

Figure 4. A typical sample process technique to concentrate strontium and actinides from a complex matrix.

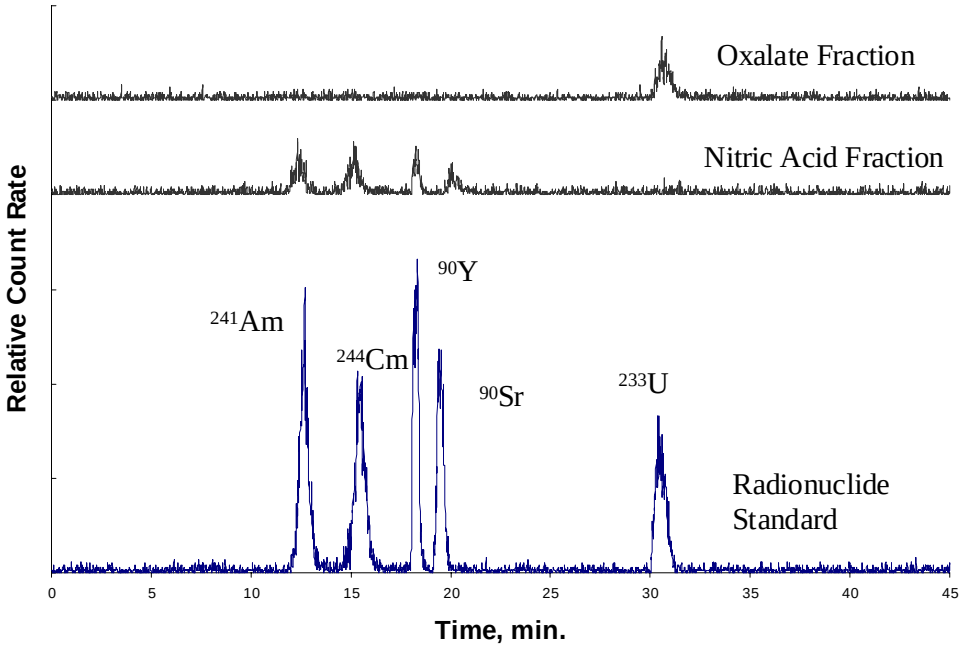

Figure 5. Examples of the chromatograms of the extracted fractions from the sample processing protocol for a complex matrix.

Applications

* Analysis of alpha emitters and pure beta emitters in environmental samples or waste samples
* Radionuclide-specific measurements in a relatively short period of time (< 4 hours)
* On-line minimum detectable concentrations on the order of 0.4 to 4 kBq/m^3 (10 to 100 pCi/g)

Future Activities

Task 1 future activities include: a protective coating for the CsI:Tl particles, a liquid scintillation flow-cell, and digital pulse shape discrimination and processing.

Task 2 is complete.

Task 3 future activities include: testing of the system on actual samples (e.g. SRS drain tank and ORNL storage tank) and sample surrogates (e.g. INEEL soil and SRS HLW tank supernate).

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